08/825,360

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     (FILE 'USPAT' ENTERED AT 14:13:42 ON 06 MAY 1999)
L1      154322 S TITANIUM OR TI
L2       91382 S TITANIUM NITRIDE OR TIN
L3       15996 S L1(7A)L2
L4       36339 S ANGSTROM#
L5         574 S L3(P)L4
L6      130384 S 438/CLAS OR 257/CLAS OR 427/CLAS
L7         447 S L5 AND L6
L8        6804 S PLASMA#(7A)(ANNEAL? OR HEAT? OR SINTER?)
L9         474 S L3 AND L8
L10         35 S L3(P)L8
L11         26 S L6 AND L10

     FILE 'EPOABS' ENTERED AT 14:36:15 ON 06 MAY 1999
L12          4 S L10
L13         11 S L5
L14         11 S L13 NOT L12

     FILE 'JPOABS' ENTERED AT 14:40:15 ON 06 MAY 1999
L15          6 S L12
L16       2484 S L3
L17          0 S L5

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 SESSION WILL BE HELD FOR 30 MINUTES
U.S. Patent & Trademark Office SESSION SUSPENDED AT 14:43:43 ON 06 MAY 199
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US-CL-CURRENT: **438/627, 643, 648, 798**

SUMMARY:

BSUM(20)

These objectives are accomplished by first sputtering a thin film of titanium which will later serve as a source for enhancing the **titanium nitride** barrier layer. Then, **titanium nitride** is sputtered over the first **titanium** layer to serve as the barrier layer for a subsequent metal deposition. At this point, the substrate thusly prepared, is introduced into a tungsten chamber where the substrate is exposed in-situ to nitrogen (N.sub.2) plasma of a specific recipe. Only nitrogen plasma is used to convert more of nitride in the first layer to more of TiN to fill up the gaps in between the grain boundaries and seal the surface. Thus, the subsequently deposited metal will not migrate through the TiN barrier layer. Furthermore, the "filling" takes place "bottoms up" from the titanium source layer so as to flush out any of the residues and contaminants, such as the etchant by-products from the earlier hole forming and cleaning processes. Thus, the eruption of unwanted products or the "volcano effect" will not take place. With the substrate having just been exposed to nitrogen plasma as described above, and the TiN barrier layer also been annealed at an appropriate temperature, tungsten metal is deposited next, still in the same chamber as the plasma. As the barrier layer is properly sealed and **annealed** by the **plasma** at the same time, it is no concern now that the by-products of the reaction WF.sub.6 +Ti.fwdarw.TiF.sub.x +by-products will be trapped in the wells of the "contact plugs" or in the side-walls of the "via-plugs" to cause any "volcano effect," as seen in the magnified plan view of one of the circular vias under a rectangularly s

US PAT NO: 5,801,098 [IMAGE AVAILABLE]
US-CL-CURRENT: **438/653, 660, 685, 688**

DETDESC:

DETD(12)

As discussed previously, layer 23 is preferably comprised of **titanium nitride** to serve as a diffusion barrier for layers 37 and 38. In the preferred embodiment, layer 23 also serves as an adhesion layer between layers 35 and 37 when layer 35 is comprised of silicon oxide and when layer 37 is comprised of tungsten because tungsten does not substantially adhere to silicon oxide. Layer 38 can be deposited before the **plasma annealing** of layer 23, but the deposition of layer 38 and the patterning of layer 39 are preferably performed after the annealing of layer 23 such that layer 23 is directly exposed to the **plasma** ambient during the **annealing** step to more effectively reduce the individual resistivity of layer 23 and the composite resistivity of layer 39.

US PAT NO: 5,739,573 [IMAGE AVAILABLE] L11: 9 of 26
US-CL-CURRENT: **257/384, 368, 382, 383, 388, 900; 438/302, 305**

DETDESC:

DETD(40)

The third embodiment has the same advantages as the first embodiment. The present embodiment is superior to the first embodiment in application to a CMOS transistor. It should be noted that the formation of a **titanium** film, the formation of a **titanium nitride** film on the **titanium** film by **plasma** nitriding, and the **heat** treatment in an argon or helium ambient which are all employed in the second e

US PAT NO: 5,652,181 [IMAGE AVAILABLE] L11: 13 of 26
US-CL-CURRENT: **438/385**; 148/DIG.136; **438/660, 768**

DETDESC:

DETD(9)

As mentioned above, it is preferred that an additional step of, forming a specific resistance capping layer superjacent the thermally processed refractory metal layer is performed, as this capping layer "locks in" the specific resistive value obtained during the thermal step. It is preferred the specific resistance capping layer comprises a nitride of refractory metal layer and specifically it is preferred that the refractory metal used to practice the present invention is titanium. When titanium is selected, it is preferred that the titanium be formed by sputtering or CVD. For the variations of titanium, this would than include sputtered **titanium**, CVD **titanium**, CVD **titanium nitride**, CVD **titanium** silicide. These CVD formed **titanium** may all be formed from TiCl4 in CVD chambers or from TDMAT in plasma and RTCVD chambers. Furthermore, for this specific example, the step of thermally processing may be selected from rapid thermal processing,

US-CL-CURRENT: **257/298, 68, 303, 306, 532**

DETDESC:

DETD(10)

Another optional post-deposition treatment may be performed on TiN formed by the preferred MOCVD process, prior to exposing the TiN layer 50 to air. A hydrogen plasma treatment reacts hydrogen with undesired carbon and/or oxygen left in the film by the decomposition of the organic precursor. At the same time, nitrogen plasma may be included in the treatment, whereby nitrogen atoms may replace carbon atoms, thus replacing TiC (or more complex compounds) with TiN. This plasma treatment may be intermittently pulsed with thin **titanium nitride** metal organic depositions within the same reactor. The **plasma anneal** reduction of organic content in the film, in combination with the more complete conversion of the **Ti** into **TiN**, results in a significantly lower resistance for the TiN layer. Lower resistance advantageously decreases the overall memory cell resistance and increases the response time of the cell. At the same time, a more purely TiN layer acts as a better diffusion barrier. The **plasma anneal** is described in the pending U.S. patent application of Sandhu, entitled "Method Of Reducing Carbon Incorporation Into Films Produced By Chemical Vapor Deposition Involving Organic Precursor Compounds," Ser. No. 08/336,260, filed Nov. 8, 1994, the disclosure of which is hereby incorporated by reference.

US PAT NO: 5,567,483 [IMAGE AVAILABLE] L11: 17 of 26

TITLE: Process for **plasma** enhanced **anneal** of **titanium nitride**

US-CL-CURRENT: **427/535, 248.1, 294, 569**

SUMMARY:

BSUM(9)

In accordance with the present invention, a **titanium nitride** film is **annealed** with a **plasma** created from a nitrogen-containing gas in a rotating susceptor reactor at a temperature less than 500.degree. C. More particularly, the present invention provides a method of **annealing titanium nitride** films with an RF generated **plasma** formed from a nitrogen-containing gas such as ammonia at temperatures significantly less than 500.degree. C. This method provides for a film having relatively low resistivity and relatively low chlorine content compared to films annealed at higher temperatures.

EP 00477990A2 Apr. 1, 1992 L12: 2 of 4

A method of enhancing the properties of a thin film on a substrate.

INVENTOR: HAIM GILBOA, et al. (1)
ASSIGNEE: APPLIED MATERIALS INC
APPL NO: EP 91116701A
DATE FILED: Sep. 30, 1991
PATENT ABSTRACTS OF EUROPE
ABS GRP NO:
ABS VOL NO:
ABS PUB DATE:
INT-CL: C23C 14/56; C23C 14/58

ABSTRACT:

    Properties of a thin film of vacuum deposited material, such as **titanium nitride**, on a substrate are enhanced by **plasma** or thermal **annealing** of the thin film without removing the film from a vacuum environment. The annealing step may be performed in the same vacuum chamber as the sputter deposition, or in a different vacuum chamber, provided the substrate can be transferred between chambers while remaining in a vacuum environment. <IMAGE>

WO 09533865A1 Dec. 14, 1995

LOW TEMPERATURE PLASMA-ENHANCED FORMATION OF INTEGRATED CIRCUITS

INVENTOR: ROBERT F FOSTER, et al. (1)
ASSIGNEE: MATERIALS RESEARCH CORP
APPL NO: US 09504127W
DATE FILED: Apr. 3, 1995
PATENT ABSTRACTS OF EUROPE
ABS GRP NO:
ABS VOL NO:
ABS PUB DATE:
INT-CL: C23C 16/02; C23C 16/34; C23C 8/36

ABSTRACT:

Using plasma enhanced chemical vapor deposition, various layers (29) can be deposited on semiconductor substrates (28) at low temperatures in the same reactor. When a **titanium nitride** film is required, a **titanium** film can be initially deposited using a plasma enhanced chemical vapor deposition wherein the plasma is created within 25 mm of the substrate surface, supplying a uniform plasma across the surface. The deposited film can be subjected to an ammonia **anneal**, again using a **plasma** of ammonia created within 25 mm of the substrate (28) surface, followed by the plasma enhanced chemical vapor deposition of **titanium nitride** by creating a plasma of **titanium** tetrachloride and ammonia within 25 mm of the substrate surface. This permits deposition film and annealing at relatively low temperatures less than 800 DEG C. When titanium is so deposited over a silicon surface, titanium silicide will form at the juncture which then can be nitrided and coated with **titanium** or **titanium nitride** using the plasma enhanced chemical vapor deposition of the present invention. Thus, the present method permits the formation of multiple layers of **titanium**, **titanium nitride**, **titanium** silicide over the surface of the s

SEMICONDUCTOR DEVICE

INVENTOR: MICHIO ASAHINA
ASSIGNEE: SEIKO EPSON CORP, et al. (30)
APPL NO: 01-292640
DATE FILED: Nov. 10, 1989
PATENT ABSTRACTS OF JAPAN
ABS GRP NO: E1116
ABS VOL NO: Vol. 15, No. 383
ABS PUB DATE: Sep. 27, 1991
INT-CL: H01L 29/46; H01L 21/90

ABSTRACT:

PURPOSE:To improve a barrier performance dramatically by including oxygen at least in one type of a barrier metal film or forming an oxide layer.

CONSTITUTION:At least one layer of metal, metal nitride, metal silicide or metal carbide is **annealed** under O.sub.2 **plasma** or ambient atmosphere which contains a trace of O.sub.2 so that the O.sub.2 may be trapped in the film or an oxide layer may be formed. For example, after the performance of contact photoetching, **TiN/Ti** is deposited with sputtering. Then, after plasma irradiation in the O.sub.2 **plasma**, it is lamp-**annealed**, then Pt/Ti is deposited so that a Cu plating interconnection 206 may be formed, thereby forming an Ni/Au flush plating layer 207 in order to improve corrosion resistance and resistance to oxidation.